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## Contract Information

Contract Number	N000140-91-06-0-6
Title of Research	Development of High-Performance Pr-Co Magnets for High-Temperature Applications
Principal Investigator	George C. Hadjipanayis
Organization	University of Delaware

## Technical Section

### Technical Objectives

- (1) Establish the phase equilibria in  $\text{Pr}_x\text{Co}_{100-x-y}\text{In}_y$  alloys with  $16 \leq x \leq 20$ ,  $0 \leq y \leq 1.5$  for the temperature range of 500 to 1100 °C. The knowledge obtained will be used to fabricate, via a simple inexpensive process, In-added  $\text{PrCo}_5$  sintered magnets with properties superior to the existing 2:17 Sm-Co magnets in the temperature range of 25 to 200 °C.
- (2) Establish the mechanism(s) of texture development in nanocrystalline  $\text{PrCo}_5$  magnets subjected to hot plastic deformation. This knowledge will allow us to improve the texture of the magnets, which ultimately will lead to the fabrication of nanocrystalline  $\text{PrCo}_5$  magnets with properties superior to the existing 2:17 Sm-Co magnets, in both the maximum energy product and coercivity.
- (3) Establish the composition and temperature boundaries of the  $\text{PrCo}_{5+\delta}$  structure in the  $\text{Pr}_x\text{M}_z\text{Co}_{100-x-z}$  alloys with  $11 \leq x \leq 16$ ,  $0 \leq z \leq 2$ ,  $\text{M} = \text{Hf}, \text{Cu}, \text{Ga}(\text{C})$  obtained via equilibrium and non-equilibrium processes. This knowledge will allow the fabrication of novel high-temperature magnets based on the off-stoichiometric  $\text{PrCo}_{5+\delta}$  structure with significantly improved properties for high-temperature applications.

### Technical Approach

The task of studying phase equilibria in Pr-Co-In system has been inspired by our recent finding that the low-melting-temperature phase(s) induced by small additions of indium can dramatically improve the densification and coercive force of  $\text{PrCo}_5$  sintered magnets; we have also found that such additions had a profound effect on the structural and magnetic properties of  $\text{PrCo}_5$  hot-deformed nanocrystalline magnets. There are no any systematic data available on the phase equilibria of Pr-Co-In and other similar systems, and the published information on four of the Pr-Co-In phases ( $\text{PrCoIn}_5$ ,  $\text{Pr}_2\text{CoIn}_8$ ,  $\text{PrCo}_2\text{In}$  and  $\text{Pr}_{12}\text{Co}_6\text{In}$ ), provided no insight on the mechanisms of the effects we observed in the In-added  $\text{PrCo}_5$  magnets. Systematic knowledge of the phase equilibria in the Pr-Co-In alloy system in the region adjacent to the  $\text{PrCo}_5$  compound was, therefore, critically important for a further development of this class of hard magnetic materials. We employed the standard technique of equilibrated alloys characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and differential thermal analysis (DTA). Upon establishing the phase equilibria in the Pr-Co-In alloys we were able to address the tasks of development of the more efficient sintered (microcrystalline) and hot-deformed (nanocrystalline)  $\text{PrCo}_5$ -based permanent magnets.

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In order to reach beyond the hard magnetic properties of the  $\text{PrCo}_5$  compound, the task of establishing the conditions for off-stoichiometric  $\text{PrCo}_{5+\delta}$  structure has been formulated. The  $\text{PrCo}_{5+\delta}$  structure, which is characterized by a disordered solid solution of the Co atom pairs in the  $\text{PrCo}_5$  structure, must exhibit an enhanced saturation magnetization  $M_s$  and Curie temperature  $T_C$ , while still maintaining the high uniaxial magnetocrystalline anisotropy (unlike the ordered solid solution, known as the  $\text{Pr}_2\text{Co}_{17}$  compound). Based on the available reference data, Hf has been first selected as the most efficient stabilizer of the disordered off-stoichiometric structure (often referred to as the "1:7" structure). In addition to Pr-Hf-Co system, which was studied most systematically, selected Pr-Co-M alloy series with  $M = \text{Al, Si, Ti, V, Cr, Cu, Ga, Ag, C-Ga, Hf-Al, Hf-Si, Hf-Ti, Hf-V, Hf-Cu}$  and  $\text{Hf-Ga}$  were also investigated.

### ***Final Report Summary***

- (1) The Pr-Co-In phase equilibria related to the indium-added  $\text{PrCo}_5$  permanent magnets have been studied systematically. The 800 °C isotherm and the  $\text{PrCo}_5$  -  $\text{PrCo}_2\text{In}$  polythermal section reveal several new compounds that were never reported for this system. One of them, the orthorhombic  $\text{Pr}_3\text{Co}_9\text{In}_2$  forms peritectically at 957 °C and it forms a two-phase equilibrium with  $\text{PrCo}_5$ . The  $\text{Pr}_3\text{Co}_9\text{In}_2$  compound is paramagnetic at room temperature and exhibits an antiferromagnetic ordering at 198 K. Also observed were the hexagonal  $\text{PrIn}_2$  compound possibly stabilized by a small amount of cobalt and an unidentified ternary phase with the approximate composition  $\text{Pr}_{45}\text{Co}_{15}\text{In}_{40}$ .
- (2) In the sintered Pr-Co-In magnets, the presence of a high-temperature liquid phase and the delayed formation of the stable  $\text{Pr}_3\text{Co}_9\text{In}_2$  phase can explain the lower sintering temperature and, at least partially, the effect of post-sintering annealing. Transmission electron microscopy (TEM) observation of the  $\text{Pr}_3\text{Co}_9\text{In}_2$  thin layers along the  $\text{PrCo}_5$  grain boundaries strongly indicates that formation of the  $\text{Pr}_3\text{Co}_9\text{In}_2$  phase is responsible for the improvement of the magnetic performance with the post-sintering annealing. Ramp annealing, which has been developed as an alternative to the isothermal heat treatment, can moderately increase the coercivity. The minimum required In content has been found to be 0.5 at. %.
- (3) An entirely new class of Pr-Co-In permanent magnets based on the  $\text{PrCo}_5$  and  $\text{Pr}_3\text{Co}_9\text{In}_2$  phases and produced via prolonged annealing of the cast alloys was discovered. Even though the magnets are obtained without the employing powder metallurgy, they are not likely to find practical applications because of their moderate magnetization and considerable content of In.
- (4) In the hot-deformed nanocrystalline Pr-Co-In magnets, in addition to the "inversed" texture of the main  $\text{PrCo}_5$  phase, a strong texture of the  $\text{Pr}_3\text{Co}_9\text{In}_2$  minority phase has been observed.
- (5) The homogeneity range of  $\text{PrCo}_{5+\delta}$  alloys at 1150 °C was found to stretch to 84.5 at. % Co. Addition of up to 1.5 at. % Hf extends this range to 85.3 at. % Co. The lattice constants, Curie temperature  $T_C$  and saturation magnetization  $4\pi M_s$  of the  $\text{PrCo}_{5+\delta}$  phase approximately follow the Vegard's law as if this phase were transitional between the stoichiometric  $\text{PrCo}_5$  phase and the hypothetical disordered  $\text{Pr}_2\text{Co}_{17}$  phase. Hafnium decreases the saturation magnetization of the  $\text{Pr}_{1-x}\text{Hf}_x\text{Co}_{5+\delta}$  phase, but has no significant effect on its  $T_C$ . The highest  $4\pi M_s$  of 12.9 kG was observed in the off-stoichiometric binary alloy  $\text{Pr}_{84.5}\text{Co}_{15.5}$ .
- (6) The solubility of Co in the  $\text{PrCo}_{5+\delta}$  structure decreases with decreasing the temperature, so only  $\text{Pr}_{1-x}\text{Hf}_x\text{Co}_5$  alloys exhibited the single-phase structure after annealing at 900 °C. Out of nineteen Pr-Co-M alloys with M other than Hf,  $\text{Pr}_{14.75}\text{Hf}_{0.5}\text{Co}_{84.25}\text{Ti}_{0.5}$ , exhibited the  $\text{PrCo}_{5+\delta}$  structure which was more stable at the lower temperatures than that on the parent

$\text{Pr}_{14.75}\text{Hf}_1\text{Co}_{84.25}$  alloy. However, the saturation magnetization of the  $\text{Pr}_{14.75}\text{Hf}_{0.5}\text{Co}_{84.25}\text{Ti}_{0.5}$  alloy was even lower than that of  $\text{PrCo}_5$ .

## Results

### Phase Equilibria in Pr-Co-In Alloy System

Figure 1 presents the phase relations determined after annealing of twenty-five Pr-Co-In alloys for up to 6 weeks at 800 °C (the dash lines in the figure represent our best judgment when the results were not fully conclusive). In a good agreement with earlier studies, the solubility of indium in the binary  $\text{Pr}_2\text{Co}_{17}$ ,  $\text{PrCo}_5$ ,  $\text{Pr}_3\text{Co}_{19}$ ,  $\text{Pr}_2\text{Co}_7$  and  $\text{PrCo}_3$  phases was found to be very low. At 800 °C, the  $\text{PrCo}_2\text{In}$  phase forms two-phase equilibria with the Co and  $\text{Pr}_2\text{Co}_{17}$  phases, but not with the  $\text{PrCo}_5$  phase. A new  $\text{Pr}_3\text{Co}_9\text{In}_2$  phase was discovered exactly on the would-be  $\text{PrCo}_2\text{In}$  -  $\text{PrCo}_5$  tie line. The x-ray diffraction (XRD) pattern of this phase can be indexed based on the orthorhombic  $\text{Sm}_2\text{Co}_9\text{In}_3$  lattice with  $a = 2.3099$  nm,  $b = 0.5070$  nm and  $c = 0.4041$  nm, though a further refinement is needed for the atomic positions in the new compound. At room temperature, the  $\text{Pr}_3\text{Co}_9\text{In}_2$  compound is paramagnetic with the magnetic susceptibility equal to  $3.8 \times 10^{-4}$  emu/g·Oe. The magnetization measured at a constant field exhibits a sharp maximum at 198 K, thus indicating an apparent transition from paramagnetic to anti-ferromagnetic state.

One of the ternary phases we often observed in the cobalt-rich Pr-Co-In alloys remains unidentified. The composition of this phase determined approximately via energy-dispersive spectrometry (EDS) is  $\text{Pr}_{45}\text{Co}_{15}\text{In}_{40}$ . At 800 °C, this "In-rich" phase forms two-phase equilibria with the  $\text{Pr}_2\text{Co}_7$  and  $\text{PrCo}_3$  phases. In addition, characterization of the  $\text{Pr}_{10.1}\text{Co}_{71.1}\text{In}_{18.8}$  alloy indicated the existence of yet another compound not reported for the Pr-Co-In system, a near-binary Pr-In phase with a hexagonal structure of the  $\text{CaIn}_2$  type ( $a = 0.490$  nm,  $c = 0.758$  nm). The binary compound of this structure is known to exist in the Yb-In system, but it was never observed in the Pr-In alloys.<sup>1</sup>

The detailed polythermal study was performed on ternary alloys situated on the  $\text{PrCo}_5$  -  $\text{Pr}_3\text{Co}_9\text{In}_2$  -  $\text{PrCo}_2\text{In}$  line; the

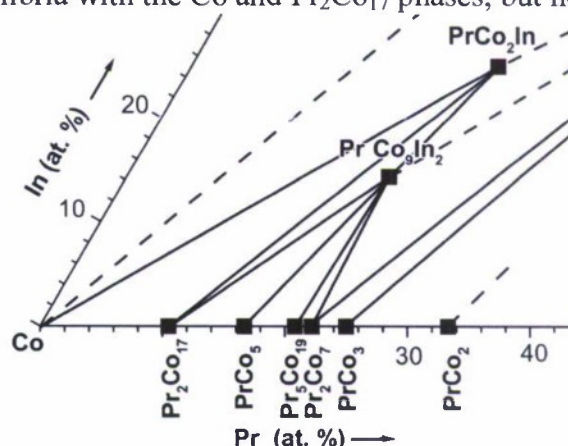


Fig. 1. Phase equilibria in the Co-rich Pr-Co-In alloys at 800 °C.

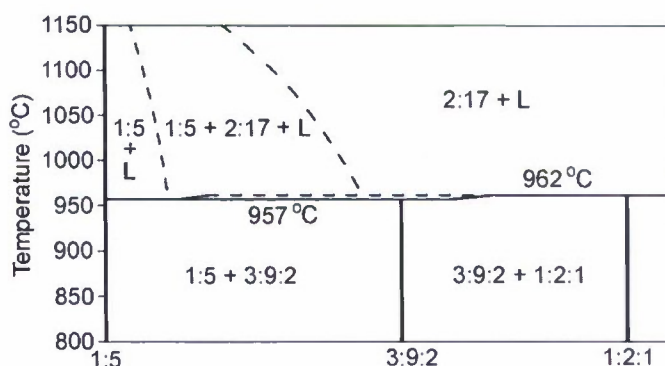


Fig. 2. Part of Pr-Co-In polythermal section passing through  $\text{PrCo}_5$ ,  $\text{Pr}_3\text{Co}_9\text{In}_2$  and  $\text{PrCo}_2\text{In}$  compounds. The compounds are abbreviated as "1:5", "3:9:2" and "1:2:1", respectively.

<sup>1</sup> We do not exclude the possibility that in our study, the compound had been stabilized by the small amount of cobalt.

resulting partial polythermal section is presented in Fig. 2. The two melting transformations,  $\text{Pr}_3\text{Co}_9\text{In}_2 \rightarrow \text{Pr}_2\text{Co}_{17} + \text{PrCo}_2\text{In} + \text{L}$  and  $\text{PrCo}_2\text{In} \rightarrow \text{Pr}_2\text{Co}_{17} + \text{L}$  are only five degrees apart.

### Microstructure and magnetic properties of sintered Pr-Co-In magnets

In order to avoid emergence of the undesirable ferromagnetic phases,  $\text{Pr}_2\text{Co}_{17}$  and  $\text{Pr}_5\text{Co}_{19}$ , the In-added magnets should follow the  $\text{PrCo}_5$  -  $\text{Pr}_3\text{Co}_9\text{In}_2$  tie line. The basic mechanisms of sintering and heat treatment of the alloys situated on this line can be understood from the polythermal phase equilibria shown in Fig. 2. The dramatic decrease of the sintering temperature with the very small In additions arises from two factors: (i) the virtual insolubility of In in  $\text{PrCo}_5$  and (ii) the low melting temperatures of the  $\text{Pr}_3\text{Co}_9\text{In}_2$  and  $\text{PrCo}_2\text{In}$  ternary phases.

Our TEM study of the annealed sintered  $\text{Pr}_{18}\text{Co}_{81.5}\text{In}_{0.5}$  magnets revealed the  $\text{PrCo}_2\text{In}$  phase in the magnet annealed at 800 °C and both the  $\text{PrCo}_2\text{In}$  and  $\text{Pr}_3\text{Co}_9\text{In}_2$  phases in the magnet annealed at 950 °C. The  $\text{Pr}_3\text{Co}_9\text{In}_2$  phase was found to be distributed around the  $\text{PrCo}_5$  grains as thin, continuous layers (Fig. 3) which are believed to contribute to the coercivity enhancement observed after the annealing.

In sintered magnets cooled from the  $\text{PrCo}_5 + \text{L}$  phase region, formation of the stable  $\text{Pr}_3\text{Co}_9\text{In}_2$  phase is suppressed not only because of the peritectic mechanism of its formation, but also by the prior formation of the metastable  $\text{PrCo}_2\text{In}$  phase, which is closer to the composition of the freshly solidified liquid phase. It seems

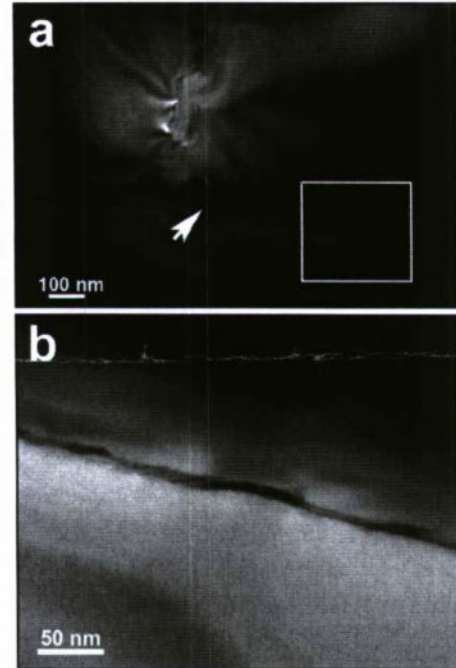


Fig. 3. (a) TEM image showing the  $\text{Pr}_3\text{Co}_9\text{In}_2$  phase as marked by an arrow in the magnet annealed at 950 °C, (b) TEM image of the grain boundary from the region marked by a rectangular frame in (a).

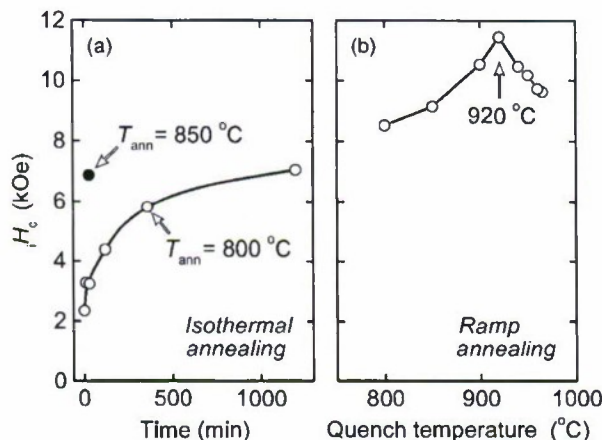


Fig. 4. Intrinsic coercivity of (a)  $\text{Pr}_{18.5}\text{Co}_{80}\text{In}_{1.5}$  magnet subjected to isothermal post-sintering annealing at  $T_{\text{ann}}$  as a function of annealing time and (b)  $\text{Pr}_{18}\text{Co}_{81.5}\text{In}_{0.5}$  magnet subjected to cooling from 965 °C at 0.5 °C/min as a function of quenching temperature. The magnets were sintered at 975 °C.

likely that the post-sintering annealing increases the coercivity  $H_c$  by replacing the  $\text{PrCo}_2\text{In}$  phase with the more favorable  $\text{Pr}_3\text{Co}_9\text{In}_2$  phase. The solidus temperature of the Pr-Co-In alloys rapidly declines with the Pr content, and so does the optimum temperature of the isothermal annealing for sintered magnets when the annealing time is fixed. In the particular case of the  $\text{Pr}_{18.5}\text{Co}_{81}\text{In}_{1.5}$  sintered magnets (Fig. 4a), it takes 20 h at 800 °C to reach the (room-temperature)  $H_c$  of 7 kOe obtained after 30 min at 850 °C.

In an attempt to develop a more efficient heat treatment protocol, we subjected the as-sintered  $\text{Pr}_{18}\text{Co}_{81.5}\text{In}_{0.5}$  magnets to slow cooling from above the solidus temperature. The  $H_c$  obtained through this procedure reached 11.4 kOe, compared to 9 - 10 kOe after the optimum isothermal annealing (Fig. 4b). Still

unexplained is an apparent magnet size effect on  $H_c$ : larger magnets subjected to any of the above heat treatment protocols tend to exhibit lower  $H_c$  values. Although this observation seems to point out the critical importance of the quenching rate, it is not clear if the underplaying mechanism is the same as in the traditional  $\text{PrCo}_5$  and  $\text{SmCo}_5$  magnets or it involves the  $\text{Pr}_3\text{Co}_9\text{In}_2$  phase.

The highest remanent magnetization  $4\pi M_r$  observed so far in the Pr-Co-In magnets, 10.7 kG, is merely 86% the saturation magnetization of the  $\text{PrCo}_5$  compound. In general, the  $4\pi M_r$  can be increased by either improving the magnet texture or maximizing the amount of the  $\text{PrCo}_5$  phase. According to our experimental data, 0.5% In is the minimum amount necessary for achieving both a reasonable density and a magnetic hardness. As we tried to decrease the amount of the non-magnetic oxide phases (by switching from a dry pressing in air to a less oxidizing wet pressing) we encountered increase of the average grain size accompanied by decline in  $H_c$ . Apparently, the oxide inclusions favor the high  $H_c$  by inhibiting the grain growth during sintering.

### ***New cast and annealed Pr-Co-In permanent magnets***

Since the equilibrium room-temperature microstructure of the alloys situated on the  $\text{PrCo}_5$  -  $\text{Pr}_3\text{Co}_9\text{In}_2$  tie line contain a highly anisotropic ferromagnetic phase and a paramagnetic phase, magnetic hardness may be expected in these alloys even without the use of a powder metallurgy. Figure 5a shows the equilibrium microstructure of alloy 6 ( $\text{Pr}_{20}\text{Co}_{70.2}\text{In}_{9.8}$ ) featuring small (smaller than  $15\ \mu\text{m}$ ) areas of the  $\text{PrCo}_5$  phase embedded into the paramagnetic  $\text{Pr}_3\text{Co}_9\text{In}_2$  matrix. The bulk alloy exhibited a moderate coercivity of 3.8 kOe; judging from this result, it is probably possible to develop "cast and annealed" permanent magnets with the  $\text{PrCo}_5$  +  $\text{Pr}_3\text{Co}_9\text{In}_2$  microstructure. However, the low saturation magnetization of such magnets and the high cost associated of the large indium additions make them unlikely candidates for practical applications.

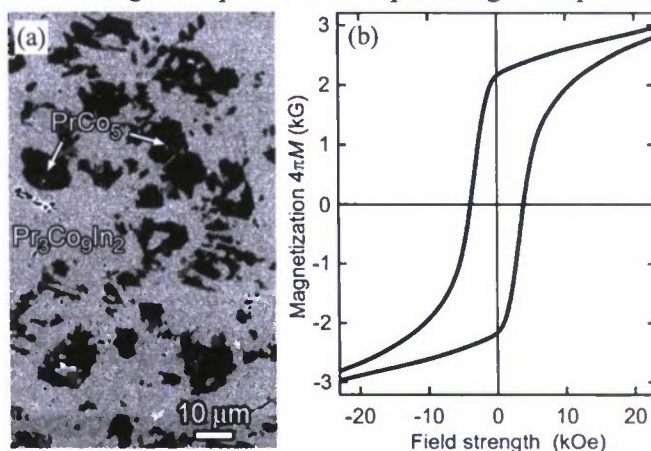


Fig. 5. (A) BSE micrograph and (b) room-temperature hysteresis loop of  $\text{Pr}_{20}\text{Co}_{70.2}\text{In}_{9.8}$  alloy annealed for 4 weeks at  $800\ ^\circ\text{C}$ . Maximum applied field is 50 kOe; data are corrected for self-demagnetizing field.

### ***Hot-deformed nanocrystalline Pr-Co-In magnets***

The nanocrystalline In-added  $\text{PrCo}_5$  magnets are primarily notable for the texture which they develop through hot plastic deformation. The tendency of the  $[001]$  axes of the  $\text{PrCo}_5$  phase to be oriented perpendicularly to the pressure direction makes this texture strikingly different from that in the In-free hot-deformed magnets, where the  $[001]$  axes exhibit the opposite tendency. Even though detrimental for the magnet performance (unless, of course, a radial deformation scheme is employed), this inversion of the texture is an interesting phenomenon which, if explained, may open new possibilities of controlling the crystallographic texture in nanocrystalline hard magnetic materials.

We have focused our study of hot-pressed and hot-deformed nanocrystalline Pr-Co-In alloys on  $\text{Pr}_{18}\text{Co}_{81}\text{In}_1$  and  $\text{Pr}_{19}\text{Co}_{77}\text{In}_4$  compositions chosen to assure different amounts of the Pr-Co-In

ternary phases. The deformation was performed at 800 °C and 950 °C, i.e. below and above the solidus temperature. The magnetization data as well as the corresponding XRD spectra suggest that the amount of the Pr-Co-In ternary phases had little effect on the texture compared to the effect of deformation temperature. On the other hand, deformation above the solidus temperature always resulted in a more pronounced texture. These results strongly suggest that not the solid ternary phases (metastable  $\text{PrCo}_2\text{In}$  and stable  $\text{Pr}_3\text{Co}_9\text{In}_2$ ) but the liquid phase is the major factor contributing to the formation of the unusual texture.

Figure 6 compares the XRD spectra of the intact and powdered  $\text{Pr}_{19}\text{Co}_{77}\text{In}_4$  magnet deformed above the solidus temperature. The (110) and (200) reflections of the intact sample are enhanced indicating, in a good agreement with the magnetization data and with our earlier report for similar alloys, that the [001] easy magnetization direction is preferentially oriented in the specimen plane (perpendicularly to the pressure direction). New is the finding that the  $\text{Pr}_3\text{Co}_9\text{In}_2$  phase in the  $\text{Pr}_{19}\text{Co}_{77}\text{In}_4$  alloy also exhibits a very strong texture. Markedly increased (800) and (10 0 0) reflections of this phase in the intact sample indicate that the [100] axes are aligned parallel to the pressure direction.

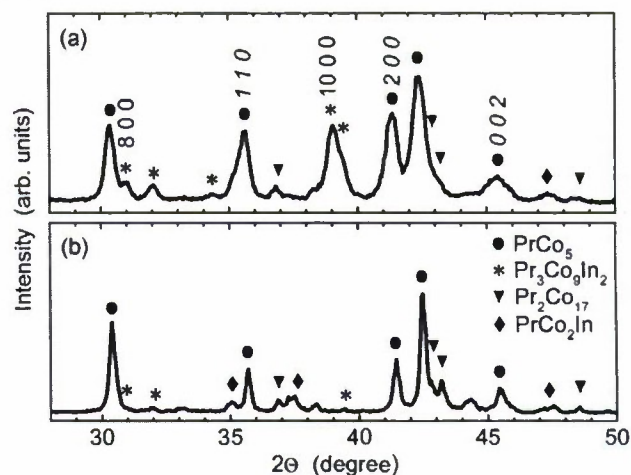


Fig. 6. XRD patterns of  $\text{Pr}_{19}\text{Co}_{77}\text{In}_4$  nanocrystalline magnets hot-deformed at 950 °C: (a) magnet cross-sectioned perpendicularly to pressure direction and (b) powdered magnet.

### Stable Pr-M-Co phases with $\text{PrCo}_{5+\delta}$ structure

Thirty-two Pr-Hf-Co alloys were analyzed in order to find the boundaries of a single-phase  $\text{Pr}_{1-x}\text{Hf}_x\text{Co}_{5+\delta}$  region. Figure 7 shows these regions at 1150 and 900 °C. In the binary Pr-Co alloys, the single-phase  $\text{PrCo}_{5+\delta}$  region stretches from 83.3 to 84.5 at. % Co, whereas in the ternary Pr-Hf-Co alloys, the Co-rich boundary extends to 85.3 at. % (the Co-poor boundary remains at around 83.3 at. %). The Hf-rich boundary of the  $\text{Pr}_{1-x}\text{Hf}_x\text{Co}_{5+\delta}$  region was found to be between 1.5 and 2 at. % Hf.

As the composition of the  $\text{Pr}_{1-x}\text{Hf}_x\text{Co}_{5+\delta}$  structure deviates from  $\text{PrCo}_5$  with increasing either  $x$  or  $\delta$ , the  $a$  lattice constant decreases and the  $c$  constant increases. The experimentally observed  $a$  and  $c$  of the binary  $\text{PrCo}_{5+\delta}$  solid solution can be reasonably well projected to  $a_{2:17}/\sqrt{3}$  and  $c_{2:17}/3$  at 89.5 at. % Co ( $a_{2:17}$  and  $c_{2:17}$  are the lattice constants of the rhombohedral  $\text{Pr}_2\text{Co}_{17}$  structure), thus confirming the concept that the  $\text{RCo}_{5+\delta}$  structures are transitional between the  $\text{RCo}_5$  and the disordered  $\text{R}_2\text{Co}_{17}$ .

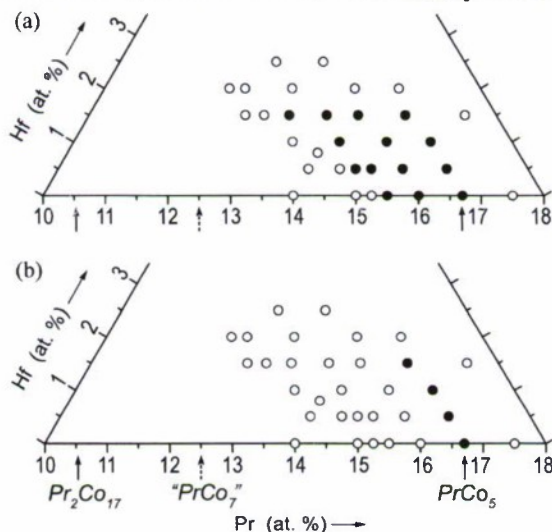


Fig. 7. Pr-Hf-Co alloys exhibiting single-phase (filled circles) and multiphase (open circles) structure after (a) annealing at 1150 °C and (b) subsequent annealing at 900 °C.

Curie temperature of the single-phase  $\text{Pr}_{1-x}\text{Hf}_x\text{Co}_{5+\delta}$  alloys depends strongly on the Co concentration increasing at the rate of 50 °C/at. % Co. On the other hand, the observed effect of Hf on the  $T_C$  is very weak. Similarly to the lattice parameters, the Curie temperature of the  $\text{PrCo}_{5+\delta}$  structure appears to follow the Vegard's law as if this structure were a solid solution between the  $\text{PrCo}_5$  and  $\text{Pr}_2\text{Co}_{17}$  compounds (assuming that the ordered and disordered  $\text{Pr}_2\text{Co}_{17}$  structures have the same  $T_C$ ).

According to the XRD characterization of selected powder samples after they had been oriented by a magnetic field, the  $\text{Pr}_{1-x}\text{Hf}_x\text{Co}_{5+\delta}$  alloys maintain the uniaxial magnetocrystalline anisotropy with the [001] easy magnetization direction throughout the whole homogeneity range. The saturation magnetization  $4\pi M_s$  of these alloys increases with  $\delta$  and decreases with  $x$ ; its increase with Co is consistent with the assumed Vegard's law. Even though the Hf addition extends the homogeneity range of this structure at 1150 °C, the highest  $4\pi M_s$  was measured for the binary alloy,  $\text{Pr}_{84.5}\text{Co}_{15.5}$ . Its  $4\pi M_s$  of 12.9 kG translates into a theoretical maximum energy product of 41.6 MGOe, an 8% increase compared to 38.4 MGOe for  $\text{PrCo}_5$  ( $4\pi M_s = 12.4$  kG).

Table 1. Phases detected by XRD in annealed Pr-Co-M alloys with M other than (only) Hf

Alloy series	M	Initial annealing for 16 h at 1150 °C	Subsequent annealing for 24 h at	
			1100 °C	1000 °C
$\text{Pr}_{14.75}\text{Co}_{84.75}\text{M}_{0.5}$	Ti	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
	V	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
	Cr	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
	$\text{Hf}_{0.5}\text{Ti}_{0.5}$	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
	$\text{Hf}_{0.5}\text{V}_{0.5}$	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
	$\text{Hf}_{0.5}\text{Cr}_{0.5}$	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
$\text{Pr}_{14.75}\text{Co}_{84.25}\text{M}_1$	$\text{Hf}_{0.5}\text{Ti}_{0.5}$	$\text{PrCo}_{5+\delta}$	$\text{PrCo}_{5+\delta}$	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$
	$\text{Hf}_{0.5}\text{V}_{0.5}$	$\text{PrCo}_{5+\delta}$	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$	
$\text{Pr}_{15}\text{Co}_{84.5}\text{M}_{0.5}$	Al	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
	Si	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
	Cu	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
	Ga	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
	Ag	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
	$\text{Ga}_{0.5}\text{Co}_{0.5}$	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
$\text{Pr}_{13.2}\text{Hf}_1\text{Co}_{85}\text{M}_{0.5}$	Al	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
	Si	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
	Cu	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
	Ga	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		
	Ag	$\text{PrCo}_5 + \text{Pr}_2\text{Co}_{17}$		

At 900 °C, the Co atom pairs are no longer soluble in the  $\text{PrCo}_5$  structure, but the solubility of the Hf atoms remains the same. The shrinkage of the  $\text{Pr}_{1-x}\text{Hf}_x\text{Co}_{5+\delta}$  region at 900 °C (and, most likely, at the lower temperatures), when it reduces to  $\text{Pr}_{1-x}\text{Hf}_x\text{Co}_5$ , must strongly limit technological options of exploring the off-stoichiometric  $\text{PrCo}_5$  alloys. Out of the several techniques used for manufacturing  $\text{PrCo}_5$  permanent magnets, only powder sintering (but without a follow-up heat treatment) may take advantage of this enhanced magnetization. The  $\text{PrCo}_5$  magnets sintered at temperature as high as 1140 °C exhibited reasonably high values of the remanence, but their coercivity was rather low. The latter may be further decreased in the off-stoichiometric  $\text{PrCo}_{5+\delta}$  magnets because of their (presumably) lower magnetocrystalline anisotropy. It seems highly desirable, therefore, to supplement any attempts of high-temperatures

sintering of the high-magnetization  $\text{PrCo}_{5+\delta}$  magnets by steps intended to inhibit an abnormal grain growth.

The structural data for nineteen Pr-Co-M alloys with M different from Hf ( $M = \text{Al, Si, Ti, V, Cr, Cu, Ga, Ag, C-Ga, Hf-Al, Hf-Si, Hf-Ti, Hf-V, Hf-Cu}$  and  $\text{Hf-Ga}$ ) are summarized in Table 1. Only in the  $\text{Pr}_{14.75}\text{Hf}_{0.5}\text{Co}_{84.25}\text{Ti}_{0.5}$  alloy, the  $\text{PrCo}_{5+\delta}$  structure was found to be more stable at the lower temperatures than that on the parent  $\text{Pr}_{14.75}\text{Hf}_1\text{Co}_{84.25}$  alloy. However, the saturation magnetization of the  $\text{Pr}_{14.75}\text{Hf}_{0.5}\text{Co}_{84.25}\text{Ti}_{0.5}$  alloy was even lower than that of  $\text{PrCo}_5$ .

### **Journal Articles (2 published, 1 submitted)**

W.F. Li, A.M. Gabay, C. Ni, G.C. Hadjipanayis, "Indium substituted  $\text{PrCo}_5$  sintered magnet: A microstructure view," *Journal of Applied Physics* **107** (2010) 063307.

A.M. Gabay, G.C. Hadjipanayis, "Phases and phase equilibria in cobalt-rich Pr-Co-In alloys for permanent magnets," *Journal of Alloys and Compounds* **500** (2010) 161–166.

A.M. Gabay, G.C. Hadjipanayis, "Stability and magnetic properties of Pr-Hf-Co alloys with the  $\text{Pr}_{1-x}\text{Hf}_x\text{Co}_{5+\delta}$  structure," *Journal of Magnetism and Magnetic Materials*, submitted.

### **Conference Presentations (1)**

A.M. Gabay, W.F. Li, G.C. Hadjipanayis, "Development of indium-added  $\text{PrCo}_5$  magnets," to be presented at the 21st Workshop on Rare-Earth Permanent Magnets and their Applications, 29 August - 2 September 2010, Bled, Slovenia.

### **Patents (0)**

There were no patent applications filed.